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# Behavior of heavy metals during gasification of phytoextraction plants: thermochemical modelling

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## Abstract

Waste such as contaminated biomass, which contain potentially high level of heavy metals, are widely available resources. One of the drawbacks of using this biomass in gasification processes is that some heavy metals might be transferred in the produced syngas, and requires then specific further cleaning steps. Thermodynamic equilibrium calculations are a relevant tool to estimate the behavior of those heavy metals to manage the syngas treatment. The calculations were made with the commercial software FactSage. Due to the several thousands of produced compounds, a specific methodology was set up to choose the stable compounds of the database for the simulations. As an illustrative example, the results of the thermodynamic equilibrium calculations of lead are presented in this paper.

**Keywords:** Biomass, Heavy metals, Thermodynamic equilibrium, Simulation, Gasification.

## 1. Introduction

Biomass is considered to be the only natural and renewable carbon resource that can effectively be a substitute to fossil fuels. This is why current researches focus on the development of the use of this alternative renewable fuel in many processes in order to produce energy. Gasification has recently been receiving increasing attention thanks to the success of the first plants for the production of electricity from biomass. In fact, gasification is the partial oxidation of biomass, which transforms the organic matter into energy carrier gas. The synthesis gas (CO and H<sub>2</sub>) allows a wide range of application: power production or biofuel. Most of research works in literature are focused on process using clean biomass as opposed to contaminated biomass which is available in significant quantities. However it is used to a much smaller extent as a source of energy due to their potentially high level of heavy metals.

An example of such biomass is phytoextraction plants which are used to extract contaminants from polluted soils. Heavy metals are then accumulated inside the roots, stems and leaves of these plants (Gupta and Sinha 2007). Following the thermochemical process of biomass gasification, these metals are found in the ash, gas and tar products which make them difficult to use and may increase risks to human health and the environment (Nzihou and Stanmore, 2013). Recent works have shown that heavy metals can have a significant influence on reaction kinetics and on thermodynamics equilibrium. The aim of this work is to contribute in understanding the behavior of heavy metals during the gasification process of contaminated biomass by modeling the

thermodynamic equilibrium. This study aims at predicting the partitioning of heavy metals in the gasification products (gas, tar or ash fractions) (Al Chami et al. 2014). This is an important scientific challenge for optimizing the thermochemical conversion processes applied to the contaminated biomass.

## 2. Materials and method

### 2.1. Biomass characterization

The biomass considered in this study is willow, which is the most used plant in phytoextraction thanks to its high absorption capacity of heavy metals. Willow is composed of 55% cellulose, 28% hemicellulose and 17% lignin (Phyllis Database, 2012). The elementary composition of willow is indicated in Table1 (Phyllis Database, 2012).

**Table 1**

Elementary composition of dry contaminated willow.

Element	mol/kg	Element	mol/kg	Element	mol/kg
C	41.25	S	0.012	Pb	$6.51 \cdot 10^{-4}$
H	58.40	F	$5.30 \cdot 10^{-3}$	Ti	$1.87 \cdot 10^{-4}$
O	27.56	Na	$5.20 \cdot 10^{-3}$	Sr	$1.59 \cdot 10^{-4}$
N	0.300	Al	$3.70 \cdot 10^{-3}$	Mn	$1.46 \cdot 10^{-4}$
Ca	0.090	Fe	$1.97 \cdot 10^{-3}$	Cu	$1.10 \cdot 10^{-4}$
Si	0.060	Ni	$1.32 \cdot 10^{-3}$	Ba	$2.91 \cdot 10^{-5}$
K	0.050	Zn	$9.48 \cdot 10^{-4}$	Cd	$1.51 \cdot 10^{-5}$
P	0.020	Cr	$8.65 \cdot 10^{-4}$	V	$3.92 \cdot 10^{-6}$
Mg	0.014	B	$8.18 \cdot 10^{-4}$	Sn	$2.52 \cdot 10^{-6}$

### 2.2. Calculations methodology

The aim of the thermodynamic modeling is to determine the nature, the state (gas, liquid or solid), speciation the amount of gasification products in given operating conditions considering that all chemical reactions reach their equilibrium. Thermodynamic models can be developed using two approaches (Basu, 2010):

- Stoichiometric Equilibrium Models, based on equilibrium constants of each reaction.
- Non-Stoichiometric Equilibrium Models, where the only inputs needed are the elemental compositions of the feeds.

The non-stoichiometric method which is often referred to as “Gibbs free energy minimization approach” is the usual approach since no chemical reaction needs to be assumed (Basu, 2010). It may be calculated using modern software provided the thermodynamic data for all compounds (reactants and products) under consideration exist. In a reacting system, a stable equilibrium condition is reached when the Gibbs free energy of the system is at the minimum. Since the thermodynamic properties of the willow components are unconventional in most software, willow has to be split into its constituent elements/molecules as input data to the software. The operating conditions chosen as initial data for the calculations are:

- initial quantity of biomass: 7 mol (biomass chemical formulae:  $C_6H_5O_4$ ),
- reactor pressure: 1 or 10 bar,
- reactor temperature: from 500 to 1000 °C (step value: 25 °C),
- gasification agent: 41 mol of  $H_2O$  (Froment et al. 2013).

Calculations were performed with FactSage 6.3 commercial software (Bale C.W. et al. 2009), which has already found applications in the field of biomass gasification modelling (Fraissler et al. 2009) (Froment et al. 2013) and includes a large database on heavy metals. FactSage uses the Gibbs free energy minimization method. For each compound, the structure of the database is as follow: available thermochemical data (standard enthalpy of formation  $\Delta H^\circ$  at 298 K, absolute entropy  $S^\circ$  at 298 K) and heat capacity polynomial dependence on temperature  $C_p(T)$  are provided for a given state (solid, liquid and gas) and a given temperature range.

As thousands of compounds and phases exist in the multicomponent system consisting of contaminated willow, a preliminary selection of the compounds which might form in gasification conditions was required: software limitations and computing time impose to take into account a maximum of 1500 compounds, while the commercial SGPS database includes more than 256 liquids, 813 solids and 894 gases. The selection procedure, based on the systematic calculation of predominance diagrams for gaseous compounds, leads to the definition of a new specific database containing a few hundreds compounds. The following methodology was applied:

1. Selection of the major elementary compounds of the main organic components of wood: C, H, N, O and S.
2. Removal of gas, liquid and solid  $C_nH_m$  compounds with  $n > 3$ .
3. Selection of all gaseous compounds existing in the contaminated willow system.
4. Removal of unstable gaseous compounds, based on predominance diagram calculations (this step is developed below).
5. Removal of gaseous compounds whose  $C_p(T)$  range validity is outside the range [500 °C-1000 °C].

Predominance diagrams were computed in order to identify the most stable compounds over specific partial pressure ranges of gaseous master species:  $O_2$ ,  $S_2$ ,  $F_2$ ,  $C_2$  and  $H_2$ . By combination with a metal element, these master species allow to account for the formation of oxides, sulfides, fluorides, carbides, hydrides and their combinations (e.g. hydroxydes, oxyfluorides, etc.). The predominance diagrams are plotted for a given fixed temperature and a total pressure. In this work, two extreme conditions of gasification process were taken into account: 500 °C/1 bar and 1000 °C/10 bar. For compounds involving O, S, H and C, all compounds shown stable on the predominance diagram were selected. Fig. 1 shows as illustrative example, the Cr-H-O predominance diagram at 500 °C and 1 bar. All those compounds were selected.

Furthermore, due to the high number of existing fluoride compounds, it has been decided to eliminate the compounds that are unlikely to form in gasification conditions

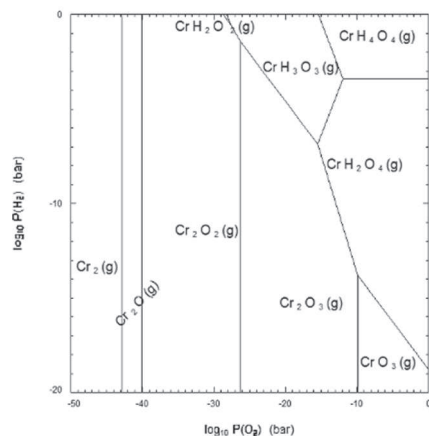


Figure 1. Cr-H-O predominance diagram (500 °C - 1 bar).

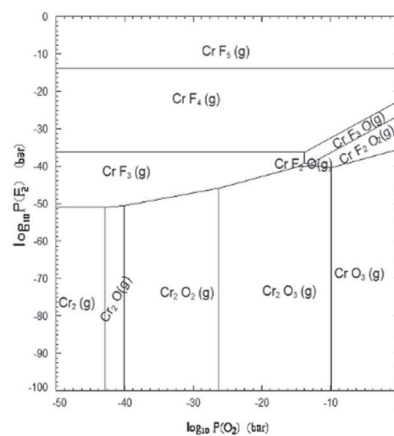


Figure 2. Cr-F-O predominance diagram (500 °C - 1 bar).

due to the low partial pressure of  $F_2(g)$ .

Preliminary calculations using a simplified biomass mixture showed that at 500 °C and 1 bar the fluoride partial pressure  $P(F_2)$  is below  $10^{-39}$  bar and below  $10^{-21}$  bar at 1000 °C and 10 bar. So all stable compounds which appeared in the predominance diagrams at a  $P(F_2)$  above those two values were eliminated from the database. For instance,  $CrF_5(g)$  and  $CrF_4(g)$  which are present in the Cr-F-O diagram (Fig.2) were not selected in the database.

### 3. Results

After the calculation and examination of 163 predominance diagrams for 20 elements (Al, B, P, Na, K, Mg, Ca, Ti, V, Mn, Cr, Fe, Ni, Cu, Zn, Cd, Pb, Si, Sr et Sn), 271 gaseous compounds were selected amongst 894 and grouped in a specific user database. Hence, the thermodynamic equilibrium calculations were performed, with the elemental composition of willow (Table 1), with the user database for the gases and the SGPS database for the liquid and solid compounds.

#### 3.1. Partial Pressure of gaseous master species and total volume of gas

The equilibrium calculations allow determining the total gas volume and the partial pressure of all the gaseous compounds. Fig. 3 shows the variation of partial pressure of gaseous master species ( $O_2$ ,  $S_2$ ,  $F_2$ ,  $H_2$ ) at two total pressures 1 and 10 bar. These pressures are related to the predominance diagrams so we can exactly determine the stable compounds and their fate at the real partial pressure of this system. The calculations confirm that the fluoride partial pressure at 500 °C/1 bar is less than  $10^{-39}$  bar and  $10^{-21}$  bar at 1000 °C/10 bar. Hence, the hypothesis regarding the selection of fluoride compounds is validated. Hence, the hypothesis regarding the selection of fluoride compounds is validated. And as expected from thermodynamic point of view, the total volume of gas increases with the temperature and the total pressure (Fig. 4).

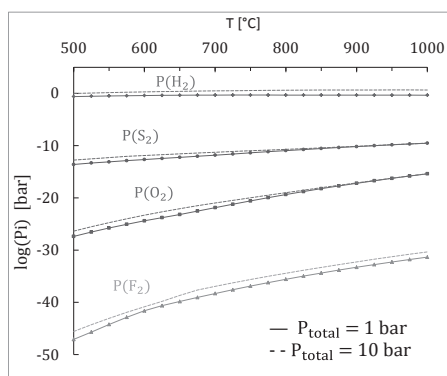


Figure 3. Partial pressure of gaseous master species at 1 and 10 bar.

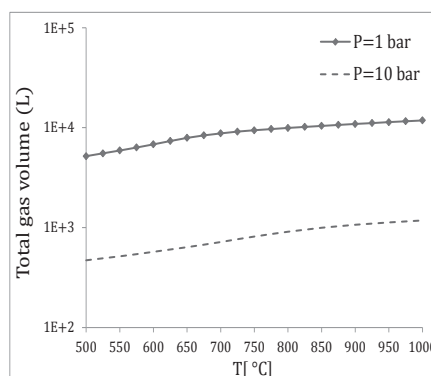


Figure 4. Total volume gas variation at 1 and 10 bar.

#### 3.2. Speciation of Pb species

As an example of heavy metals, the behavior of lead is discussed in this work, because of its high volatility.

The thermodynamic calculations are used to identify the speciation of all biomass elements. Fig. 5 presents the speciation of the lead at a total pressure of 1 bar. Above 700 °C, liquid Pb vaporizes to form mainly Pb(g) and PbS(g), as well as small quantities of PbO(g). The calculations also show that, even if the PbO(g) amount notably increases at high temperature, this compound remains a minor component of the gas phase in the whole temperature range.

### 3.3. Pressure effect

The total pressure effect from 1 to 10 bar is reported in Fig. 6. As expected from thermodynamic stand point, increasing the total pressure delays volatilization of most Pb species. At 1 bar the whole amount of lead volatilizes at 700 °C, while for a total pressure of 10 bar it volatilizes at 800 °C. A comparison of the speciation of lead at 1 bar and 10 bar (Fig. 5 and Fig. 6), evidences the presence of PbS in the condensed phase at high pressure and low temperature.

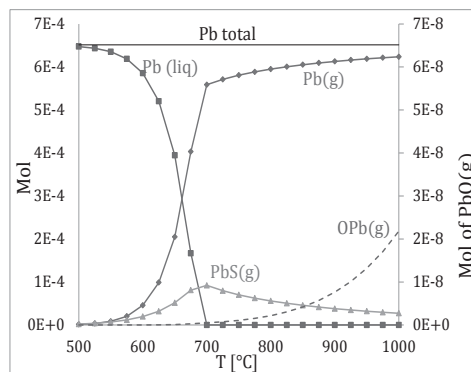


Figure 5. Speciation of Pb calculated at 1 bar.

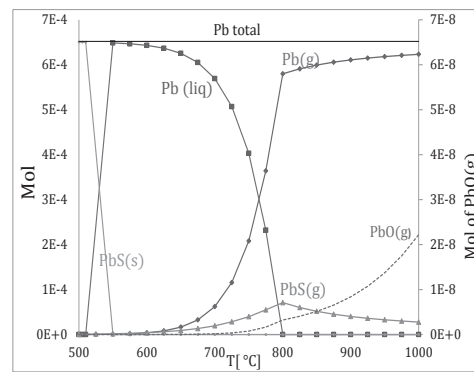


Figure 6. Speciation of Pb calculated at 10 bar.

### 3.4. Concentration effect

As willow is a plant which has a high potential to accumulate heavy metals, the concentration of Pb can vary for a plant to other depending in the soil contamination. The initial lead concentration in the willow used in this work is 135 mg.kg<sup>-1</sup>. Nzihou et al. (2013) summarized the different limits concentration of heavy metals in phytoextraction plants: the concentration of Pb can vary between 55 and 300 mg.kg<sup>-1</sup>.

Fig. 7 shows that doubling the initial concentration of Pb increases the temperature at which the whole amount of Pb volatilizes by 30 °C. Conversely, a speciation of inorganics during wood gasification realized by Froment et al. (2013) using a lower lead concentration (1 ppm) shows that the whole amount of Pb volatilizes at 500 °C. This is linked with the increase of the total volume of gas with temperature (Fig. 4): a higher volume of gas is required to evaporate a higher amount of Pb. No other concentration effect was evidenced.

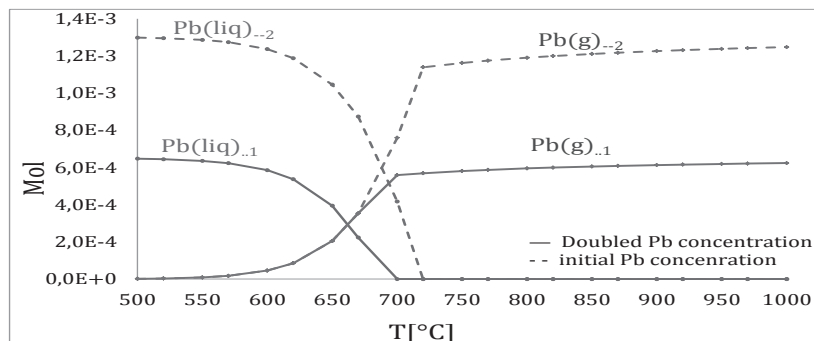


Figure 7. Effect of lead concentration (135 and 270 mg.kg<sup>-1</sup>)

#### 4. Conclusions

Equilibrium calculations using a compound thermodynamic database were carried out to simulate contaminated biomass gasification. Due to the high number of compounds related to biomass composition, a selective methodology was applied in order to focus on the most relevant gaseous compounds.

An example dealing with the behavior of lead during gasification is provided. It shows that, at concentration of about 135 mg/kg in a contaminated willow biomass, lead is mostly found in the gaseous phase under its metal form, and in smaller quantity as sulfur and oxide.

Ongoing work is considering the behavior of other metal species (Transition metals, Alkali and alkaline earth metals).

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